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A STUDY OF THE FUNDAMENTAL MECHANISM  
OF CHEMICAL DISPERSION OF OIL SPILLS

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# A STUDY OF THE FUNDAMENTAL MECHANISM OF CHEMICAL DISPERSION OF OIL SPILLS

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## SUMMARY

This report is of a research program, the object of which was to elucidate the fundamental mechanism by which commercially available chemical dispersants cause the dispersion or emulsification of spills of crude oils on ocean surfaces. The program consisted of two approaches.

First was an examination by eye, by still photography, by conventional video photography, and by high speed video photography of the microscopic dispersion process which occurs when a drop of dispersant lands on an oil slick and induces dispersion. This study showed that the process is sufficiently slow that it can be "captured" by 30, cine or video photography at frames per second and even by rapid motor-driven still photography. Some examples are given showing the dispersion event which appears to consist of a "burst" of oil (probably containing dissolved surfactant and thus of low oil-water interfacial energy) emulsifying into the water column as a cloud of variable-sized oil droplets.

Second was a study of the amount of oil dispersed as a result of placement of drops of dispersant of known size and number on an oil slick. To accomplish this a novel method of generating small dispersant drops was devised. The results tended to confirm earlier postulations that dispersion is a "two regime" process. First is a "performance limited" regime in which one volume of dispersant is able to disperse a fixed number of volumes of oil (eg. 50 volumes). Second in the case of thinner slicks is a less effective "first order" or "access-limited" regime in which one volume of dispersant is able to disperse only a fixed fraction of the remaining oil, (eg. 50%).

The implications of these findings for countermeasures, research and emergency planning are discussed.

## RÉSUMÉ

On présente le compte rendu d'un programme de recherche consacré à l'étude du processus par lequel les dispersants commerciaux provoquent la dispersion ou l'émulsification du pétrole brut à la surface de l'océan. Pour ce faire, on a procédé de deux façons.

Premièrement, on a étudié le processus de dispersion qui se déroule à l'échelle microscopique lorsqu'une goutte de dispersant tombe sur une nappe de pétrole: on a suivi le processus à l'oeil nu et on a examiné des images prises au moyen d'un appareil photographique, d'une vidéo caméra ordinaire, et d'une vidéo caméra à haute vitesse. On a constaté que le processus est suffisamment lent pour qu'on puisse le suivre avec une ciné caméra ou une vidéo caméra à 30 images par seconde et même avec un appareil photographique rapide à moteur. Dans les exemples présentés, la dispersion apparaît comme une "bouffée" de pétrole (contenant probablement du surfactant dissous, de sorte que l'énergie à l'interface pétrole-eau est faible) qui s'émulsifie dans l'eau en formant un nuage de gouttelettes de différentes grosseurs.

Deuxièmement, on a cherché à voir quelle quantité de pétrole est dispersée dans une nappe soumise à l'action d'un nombre déterminé de gouttelettes de dispersant du grosseur connue. Pour ce faire, on a mis au point une nouvelle méthode qui permet de produire de petites gouttes de dispersant. Les résultats de ces travaux tendent à confirmer ce qu'on avait supposé, soit que la dispersion est un processus qui peut se dérouler suivant deux régimes différents: un régime "limité par l'efficacité" du dispersant, dans lequel un volume donné de dispersant disperse un nombre déterminé de volumes de pétrole (p. ex., 50), et un régime moins efficace, "limité par l'accès", selon lequel un volume donné de dispersant ne peut disperser qu'une fraction déterminée du pétrole qui reste (p. ex., 50%).

On parle de la signification que prennent ces observations dans le contexte des mesures correctives prises en cas de déversement, de la recherche et de la planification des mesures d'urgence.

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## 1. INTRODUCTION

Recent research studies of chemical dispersion of oil spills have shown that a major concern is the possible lack of effectiveness of commercially available products when applied to experimental spills. This issue has been discussed by Nichols & Parker (1985), Mackay et al. (1985), in a recent Symposium Proceedings (Allen 1984), and in a series of papers in the bi-annual Oil Spill Conferences, notably those by Delvigne (1985), Lichtenthaler and Daling (1985) and Lewis and Byford (1985). Whereas dispersants are usually very effective under laboratory conditions, they are often disappointingly effective under oceanic conditions. This may be due primarily to the mis-application of dispersants at sea, for example underdosing thick slicks and overdosing sheen or applying insufficient dosage. It is clear that insights into the performance of dispersants (and thus into their more effective deployment) can be obtained by conducting basic studies of the mechanism of the dispersion process. This implies observing the process directly, possibly with the aid of video photography, and making measurements of the amount of oil dispersed under conditions in which there is controlled and reproducible exposure of oil to dispersant. This project describes an attempt to satisfy these objectives.



## 2. EXPERIMENTAL

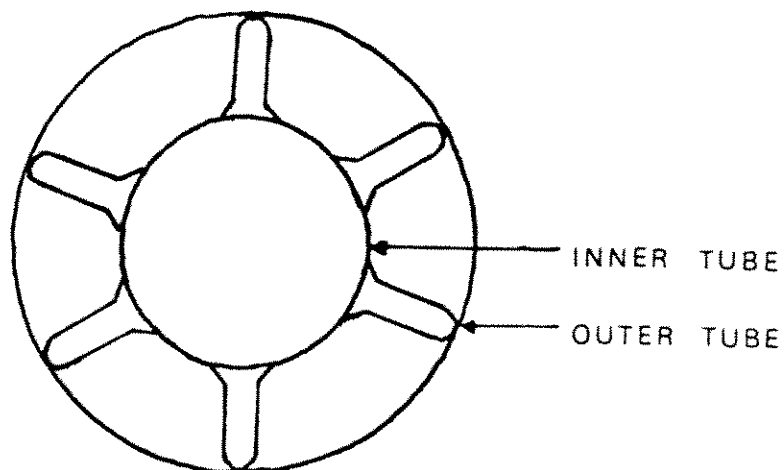
The dispersion apparatus used in this study was the Double Tube Apparatus described by Mackay et al. (1984, 1985, 1986). The advantage of this apparatus is that it enables the dispersion process to be seen directly from above and below. In principle, the aim is to hold a slick of oil, of variable but defined thickness, on a water surface where it is subject to radial shear currents in the underlying water. Dispersant is then introduced, drop by drop, on the oil surface. Dispersion can be observed and measured by analysis of the water, or more easily by measuring the remaining quantity of oil.

As shown in Figure 2.1 the apparatus consists of a 5.4 cm inner diameter by 19 cm high glass tube fitted into a 9.2 cm inner diameter by 29 cm high glass tube. Six radial glass supports on the inner tube ensure that it remains centred within the larger tube and stable during flow. Both tubes were tapered at the lower end. The inner tube is connected to a 7 mm inner diameter tube and the outer tube to a 2.5 cm inner diameter opening. This opening is sealed with a rubber stopper with one hole to accommodate the 7 mm tube of the inner tube and the other to accommodate another 77 mm inner diameter glass tube which is sealed at the end and is perforated with small holes to allow the flow of water into the apparatus to be evenly distributed. This results in a uniform flow of water up between the two tubes, radially inwards at the surface, and along to and down the inner tube.

The apparatus is connected to a constant level tank with Tygon tubing as shown in Figure 2.2 by adjusting the valves which control the water flowrates in and out of the apparatus. These valves allow the water level in the apparatus to be regulated.

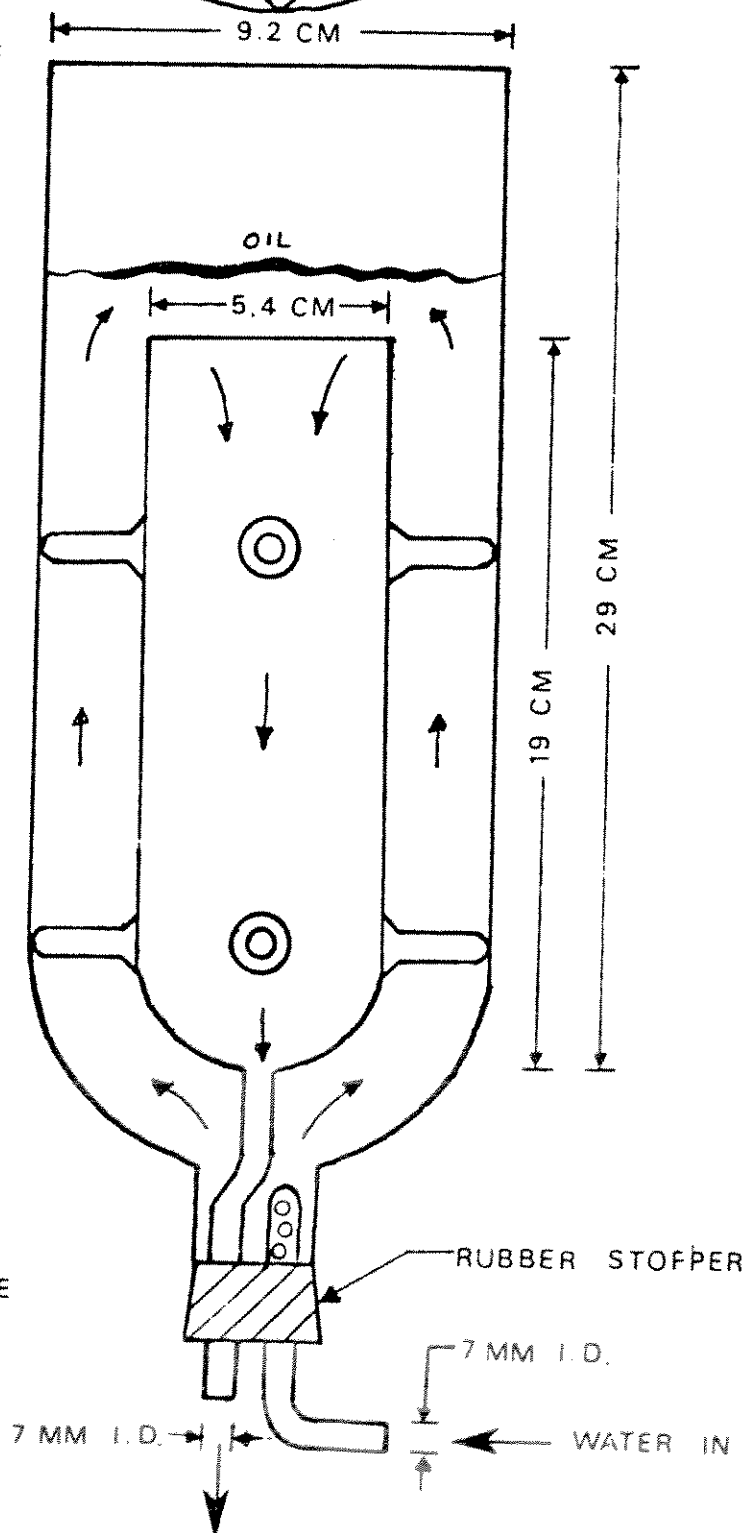
For a typical dispersion test, a steady flow of water (salinity 33 g/L) at 2.5 L/min was started through the double tube apparatus, and the water level

TOP VIEW:



3.

SIDE VIEW:



**FIGURE 21**  
DOUBLE TUBE  
APPARATUS

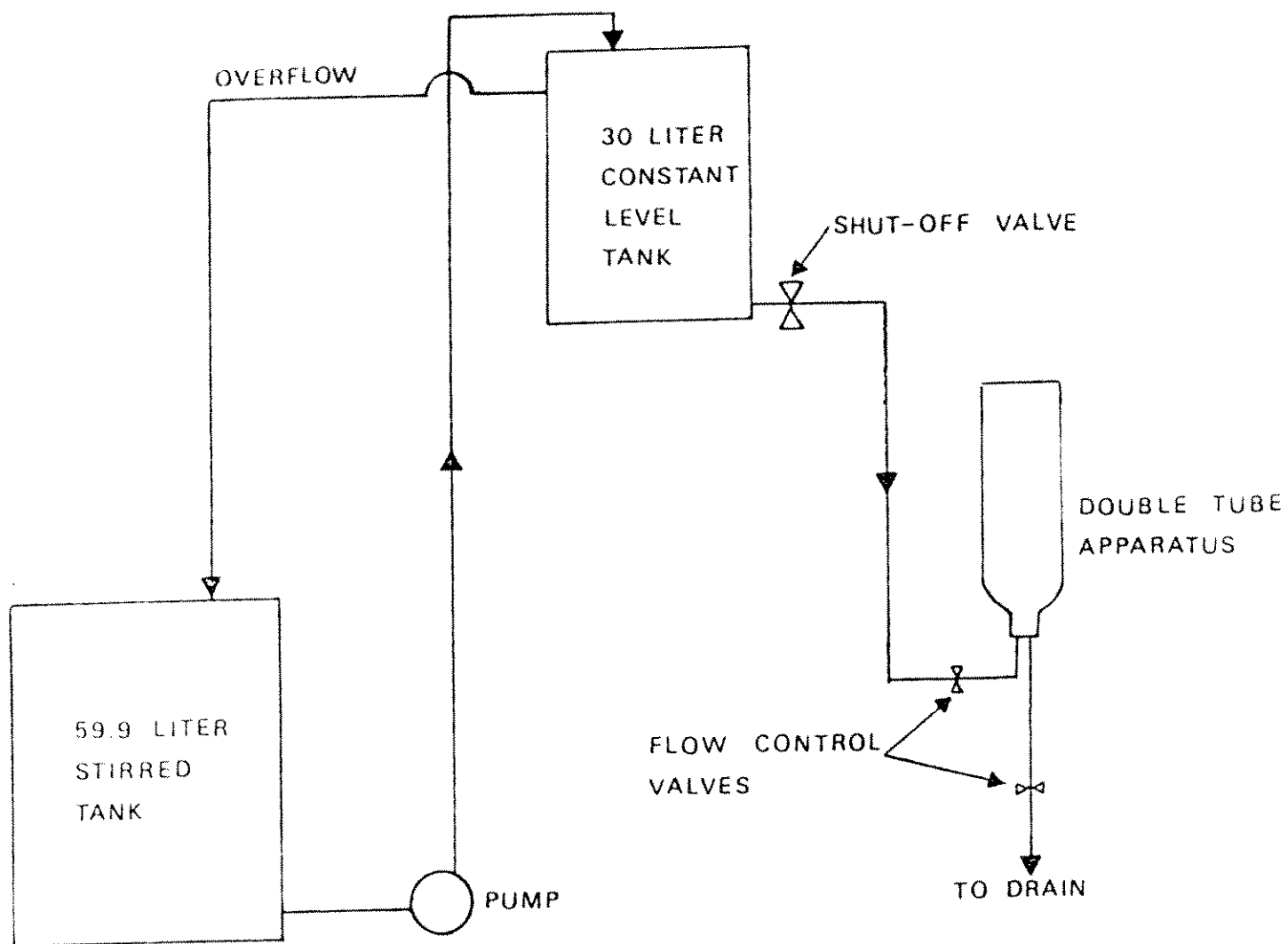


FIGURE 2.2  
APPARATUS

was set at 0.5 to 1.0 cm above the top of the inner tube. A known volume of oil was added to the water surface from an appropriate pipette. The dispersant was then added, regulating the drop size to the oil surface from a syringe with the tip located at a height of 1 to 2 cm above the slick.

The minimum drop diameter which could be delivered with the pipette was about 2 mm. This is a factor of five larger than a typical drop delivered from an aircraft spray system. In order to reduce the drop size, a modified dispersant delivery system was devised. This was based on a system used to generate polymer encapsulated insulin-producing cells for in vitro implantation in victims of diabetes (Sefton 1986). The system, illustrated in Figure 2.3 consisted of a syringe pump connected to a dispersant reservoir and a nebulizing unit. The pump delivered dispersant at a desired rate to a hypodermic needle which was mounted coaxially within a tube through which air was flowed at a controlled rate. By increasing the air flowrate, the drops of dispersant were sheared from the needle at smaller diameters, thus it became possible to generate dispersant drops down to a diameter of approximately 0.4 mm.

The average drop diameter was determined by counting the number of drops delivered during the discharge of a known volume of dispersant.

To measure the amount of oil dispersed, the inlet and outlet flow of water were clamped shut and the oil was allowed to settle for 2 minutes. A known mass of 2.5 cm-square oil 3M sorbent was placed on the oil/water surface to soak up the oil. The sorbent was then weighed to determine the amount of oil remaining and dispersed. Allowance was made for the amount of water absorbed by the sorbent.

To assist in interpreting the data obtained, two series of photographic records were obtained of the dispersion process.

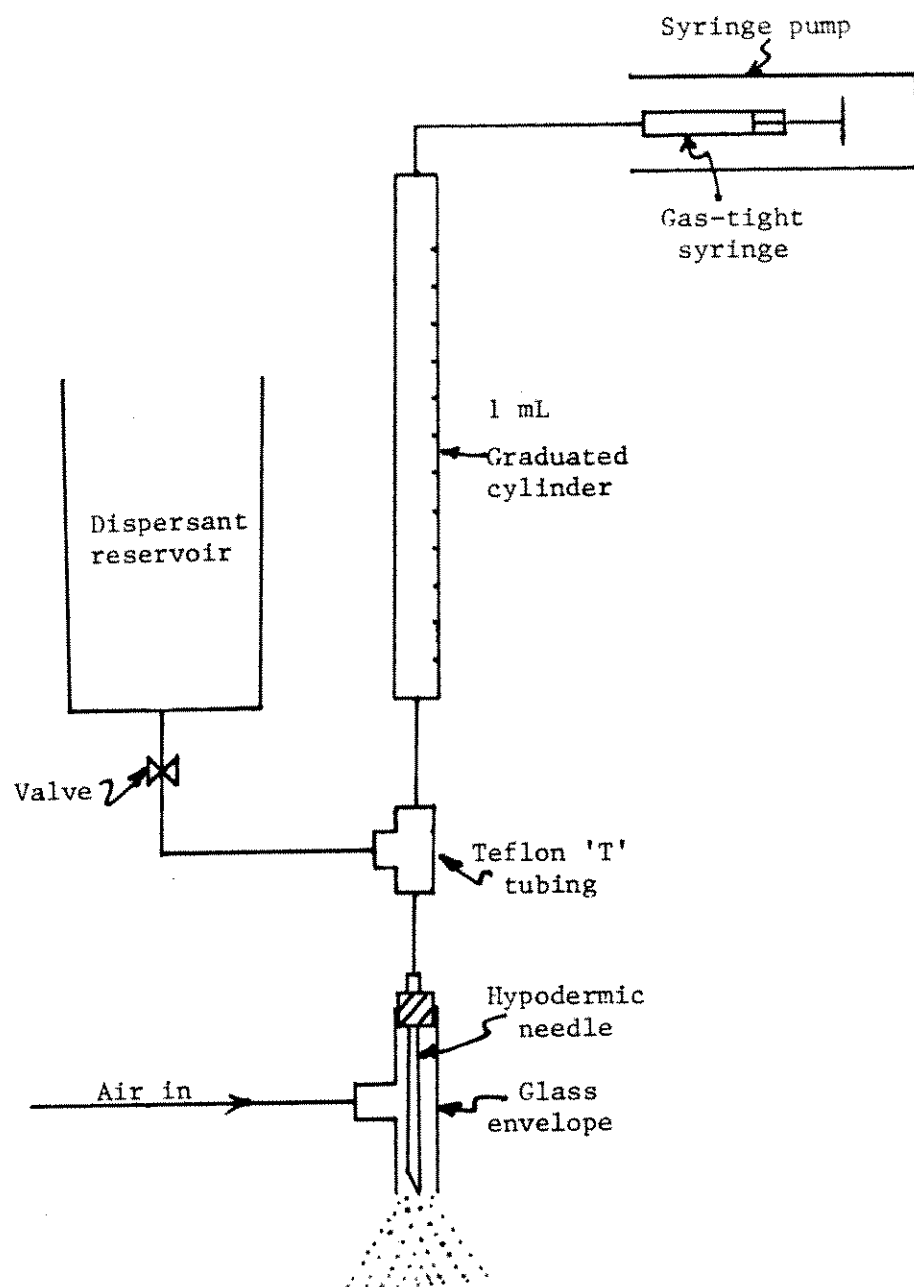


Figure 2.3 The Schematic Diagram of a Spraying Unit

In February 1986 a series of dispersion tests was conducted at the University of Alberta with the assistance of Dr. Peter Smy and Dick Hales. The system used was a Motion Analysis System Model SP 2000 consisting of a camera with a solid state image sensor capable of scanning at a high rate of frames per second. In this work a speed of 200 frames per second was used. The image was processed and stored on video tape.

Three oils were tested, EPS Standard, Sable Island Crude Oil and Arabian Heavy Crude Oil. The dispersants used were Corexit 9527 and BP MA 700. Density and viscosity data are given in Table 2.1.

Table 2.1: Density and Viscosity of Oil at Room Temperature.

Crude	Density (g/mL)	Viscosity (mPa.s)
EPS	0.8360	4.8
Sable Island	0.8420	2.4
Arabian Heavy	0.8950	64.4

The test conditions are given in Table 2.2.

Table 2.2: Dispersion Tests at the University of Alberta

Run No.	View*	Oil	Oil Vol	Dispersant
1	T	EPS Std.	5 mL	MA700
2	T	EPS Std.	5 mL	9527
3	T	EPS Std.	3 mL	9527
4	T	EPS Std.	3 mL	MA700
5	T	Sable Island	5 mL	MA700
6	T	Sable Island	5 mL	9527
7	T	Arabian Heavy	5 mL	9527
8	T	Arabian Heavy	5 mL	MA700
9	T	Arabian Heavy	3 mL	MA700
10	T	Arabian Heavy	3 mL	9527
11	T	Arabian Heavy	10 mL	9527
12	T	Arabian Heavy	10 mL	MA700
13	T	ETS Std.	10 mL	MA700
14	T	ETS Std.	10 mL	9527
15	T	Sable Island	5 mL	9527
16	T	Sable Island	5 mL	MA700
17	T	Sable Island	5 mL	MA700 Repeat
18	T	Sable Island	5 mL	MA700 Repeat
19	B	Sable Island	5 mL	MA700
20	B	Sable Island	5 mL	9527
21	B	Arabian Heavy	5 mL	9527
22	B	Arabian Heavy	5 mL	MA700
23	B	EPS Std.	5 mL	MA700
24	B	EPS Std.	10 mL	9527
25	B	Sable Island	10 mL	9527
26	B	Sable Island	3 mL	9527
27	B	EPS Std.	3 mL	9527
28	B	EPS Std.	5 mL	9527 (3 drops)
29	B	EPS Std.	10 mL	9527 (3 drops)
30	B	EPS Std.	5 mL	9527 (3 in 1 shot)
31	B	EPS Std.	10 mL	9527 (3 in 1 shot)
32	B	EPS Std.	5 mL	9527 (1 drop, 100 µl syringe)
33	B	EPS Std.	5 mL	9527 (100 µl gas syringe)

\* T from top, B from bottom.

Some additional conventional cine and still photography was conducted at the University of Toronto using a Kodavision Series 2000 8 mm video camera and an Olympus OM1 camera fitted with a motor drive.

### 3. RESULTS AND DISCUSSION

The photography showed that after the dispersant drops landed on the oil surface there was a delay of some seconds as penetration and some mixing occurred. If the dispersant drop reached the water surface intact, it caused a sudden rupture of the interface and rapid herding. Presumably the total water-dispersant-air interfacial energy is less than the water-oil-air energy. Dispersant drops were observed to enter the water column and sink. Regions of oil-water interface were observed to be unstable and subject to emulsification, especially when agitated. Presumably the oil-water interfacial energy or tension becomes very low and resistance to deformation becomes negligible.

The University of Alberta results were stored on video tape and have been supplied to the scientific authority. Since the record is black and white it is often difficult to discriminate between dispersant and oil. A colour record is preferable. The dispersion process may take a total of one minute thus very high speed recording can result in prolonged viewing times. The ideal recording speed is probably about 60 to 90 frames per second. Rapid motor-driven still photography with a 35 mm camera is particularly attractive because it gives a very clear print of various stages of the dispersion event.

Figures 3.1 to 3.8 are annotated prints of various stages of a typical dispersion process.

The times necessary for the dispersant drop to penetrate through the oil layer and reach the water surface are given below in Table 3.1.



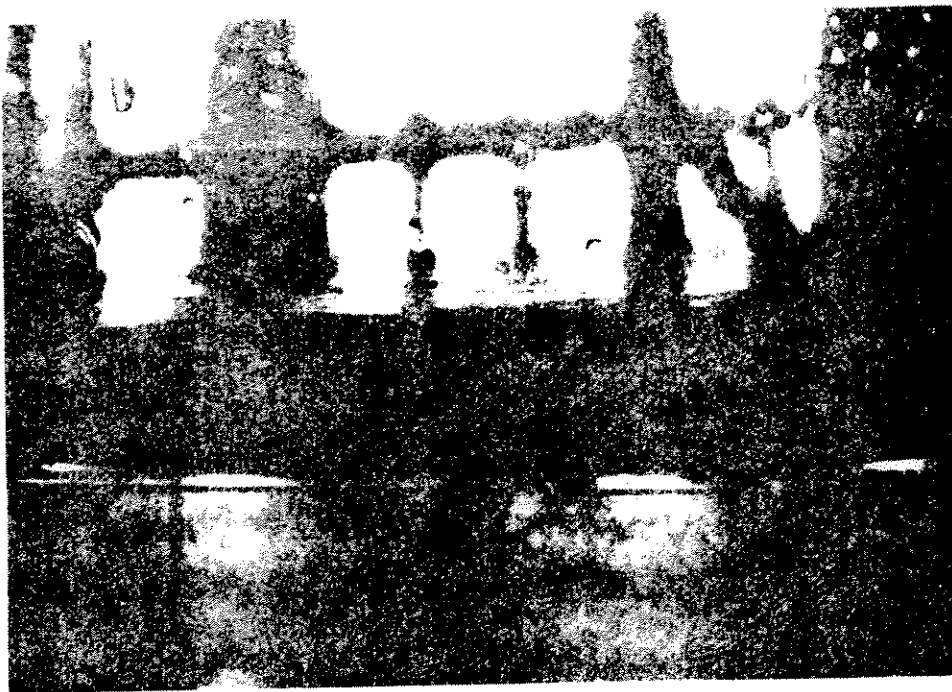


Figure 3.1  
Initial oil slick  
of EPS crude oil  
0.75 mm thick



Figure 3.2  
Dispersant  
(dyed red) being  
added. The pipette  
tip diameter is  
0.5 mm.



Figure 3.3  
 $t = 1.5 \text{ sec}$   
Time 1.5 s  
No sign of  
dispersion



Figure 3.4  
Time = 2.0 s  
First sign of  
interfacial  
activity



Figure 3.5  
 $t = 2.5 \text{ sec}$   
Considerable  
interfacial  
activity including  
vortices



Figure 3.6  
Time = 3.0 s  
Continuing inter-  
facial activity



Figure 3.7  
 $t = 4 \text{ sec}$   
Continuing  
dispersion

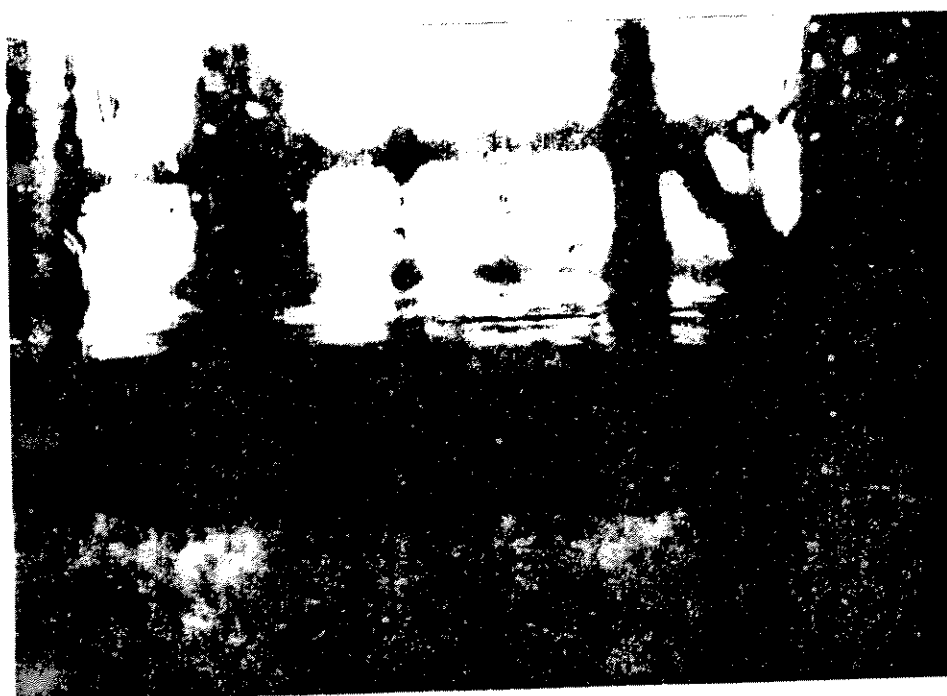


Figure 3.8  
Continuing  
activity but the  
interface is  
beginning to  
stabilize

Table 3.1: Times (seconds) for the Dispersant to Sink Through the Oil Phase to the Oil-Water Interface.

Oil	Slick Thickness (mm)	Corexit - 9527	BP - MA700
EPS	0.45	1.92	2.69
	0.75	5.72	---
	1.50	2.30	1.30
Sable Island	0.75	0.5	0.5
Arabian Heavy	0.45	19.7	20.7
	0.75	25.98	22.21
	1.5	25.6	22.20

These results indicate that oil viscosity is the key determinant of sinking time. A 1 mm slick of these three oils will experience times of approximately:

EPS	:	3 seconds	Viscosity: 4.8 m.Pa.s
Sable Island:		1 second	Viscosity: 2.4 m.Pa.s
Arabian Heavy:		25 seconds	Viscosity: 64 m.Pa.s

Thus it appears that the time for penetration of a 1 mm slick (in seconds) is approximately half the viscosity (in mPa.s). An implication is that for very viscous oil slicks, eg. 1000 or 10000 mPa.s or centipoise, the penetration time may be many minutes or even hours. During that time there is a possibility that the dispersant will be washed off the oil. It is suspected that oils may form a "skin" adjacent to the water interface which will further impede migration of surfactant to the interface.

It is believed that dispersant drop diameter has an effect on dispersing efficiency (Mackay et al. 1985). To investigate this a series of tests was

conducted varying the drop diameter from 2.2 to 3.0 mm dropping the dispersant from the needle. The results are given in Figure 3.9.

In the early range when less than 30% of the oil slick was dispersed there was no effect of dispersant drop size. At higher percentages, ie. when the slick became thinner than 0.30 mm there was a definite effect for a larger number of smaller drops to be more effective. But in this second regime the slopes of the lines decrease and the dispersant is clearly less efficient.

In the early regime each volume of dispersant dispersed approximately 50 volumes of oil, but this ratio dropped to about 20 at higher dispersant amounts. This behavior is consistent with the "performance" and "access" regimes discussed by Mackay et al. (1985).

These results suggest that each drop of dispersant is able to disperse approximately 50 times its volume of oil until the oil slick thins to the point that the volume of oil which is to be accessed extends over a region of diameter 10 to 12 times the drop diameter. As the slick thins the volume dispersed per drop falls in a first order manner. This diameter factor (here 10 to 12) was described earlier by Mackay et al. (1985), a value of 5 being used to fit data from a variety of experimental slicks.

Figure 3.10 gives the results in the range 0.5 to 1.5 mm diameter. These results are not strictly comparable with those in Figure 3.9 because the delivery velocity was different. These results are similar in nature showing an initial near linear behaviour but with a reduction in amount dispersed as the dosage increases.

It appears that smaller dispersant drops consistently give better effectiveness. An interpretation of this is that to be effective the dispersant must be fully dissolved in the oil and thus able to migrate to the

Figure 3.9: Effect of Dispersant Drop Size on Dispersion

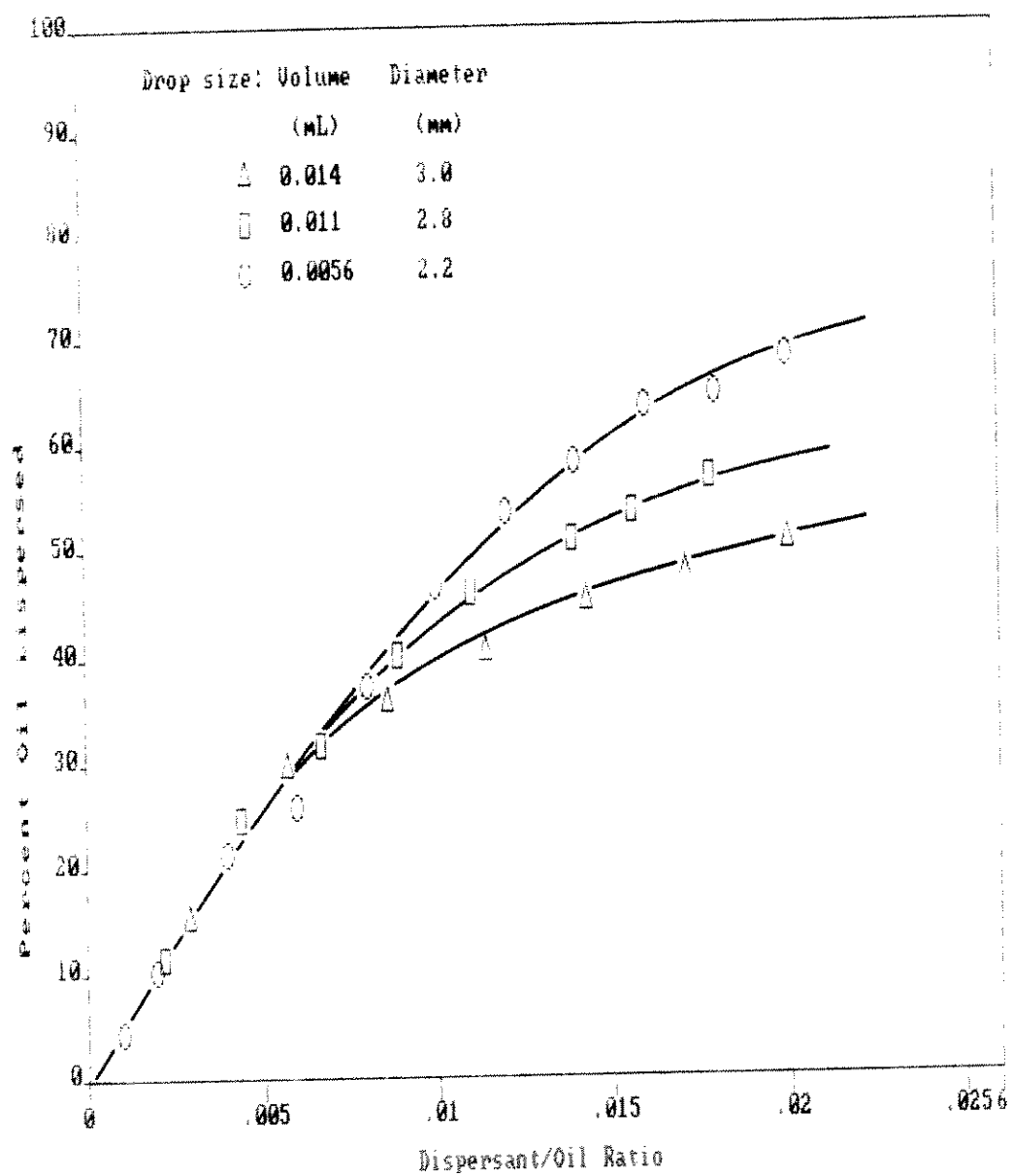
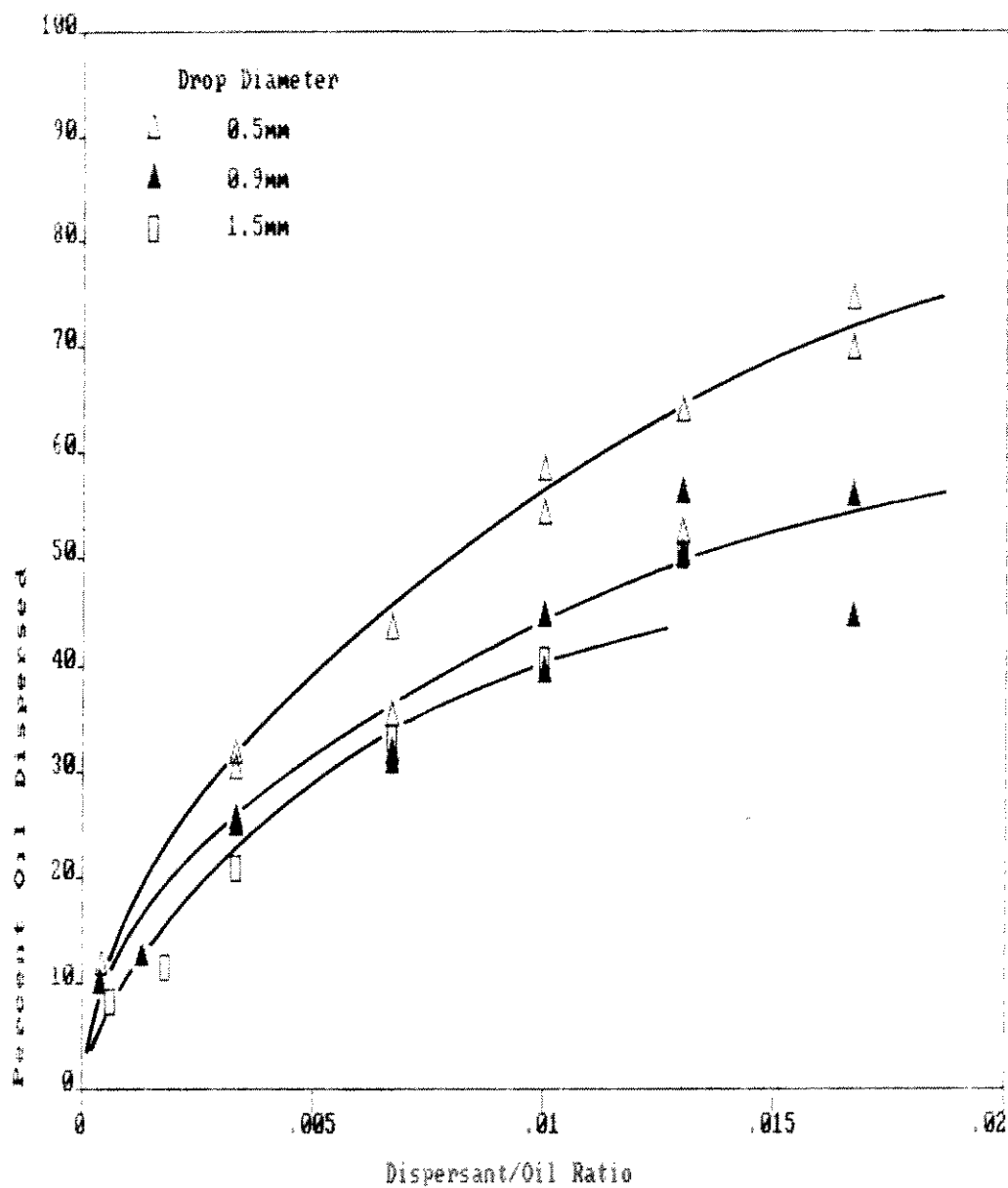


Figure 3.10: Effect of Dispersant Drop Size on Dispersion  
- Spraying.



Initial oil slick thickness = 0.45 mm  
Dispersant = Corexit 9527  
Oil = EPS Standard



oil-water interface in molecular form. Smaller drops, with a larger area/volume ratio, dissolve more rapidly and thus approach miscability more completely. Larger drops, especially those of diameter comparable to the slick thickness, dissolve more slowly and may penetrate the oil slick and reach the oil water interface in a near-intact form. They can then cause heading, or they may continue to fall on into the water phase as a dispersant drop, slowly dissolving into water. In either case, effectiveness is reduced.

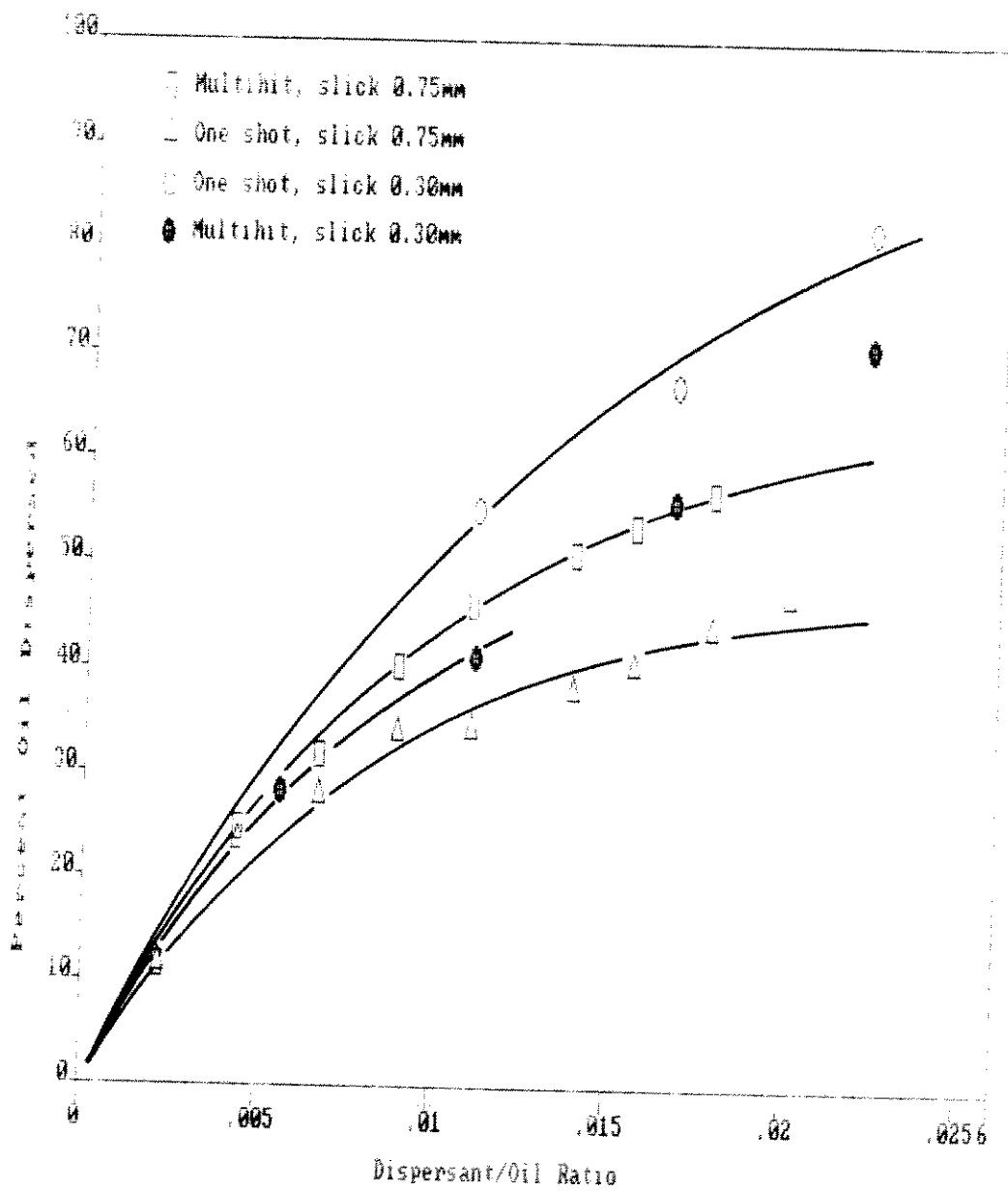
Figure 3.11 and 3.12 show the results of applying the Corexit 9527 to slicks of EPS oil of varying thickness from 0.30 and 0.75 mm. Two methods of applying the dispersant were used:

- (i) Multi-hit application in which the dispersant drops were added at intervals of 30 seconds.
- (ii) Single-hit or "one-shot" application in which the drops were added in immediate succession.

Figure 3.11 shows that the best results were obtained by one-shot application to the thinner slick, but that multi-hit application was better on the thicker slick. Figure 3.12 shows consistently better multi-hit performance. It is possible that these results reflect mainly an improved ability of the operator to place the dispersant drops on the oil surface (as distinct from placing them inadvertently on the water surface) when the application is slower and the oil has more time to assemble into a slick. It should be noted that these dispersant drops are large compared to the drops which would be generated by a dispersant-spraying aircraft, ie. 3 mm vs. 0.4 mm.

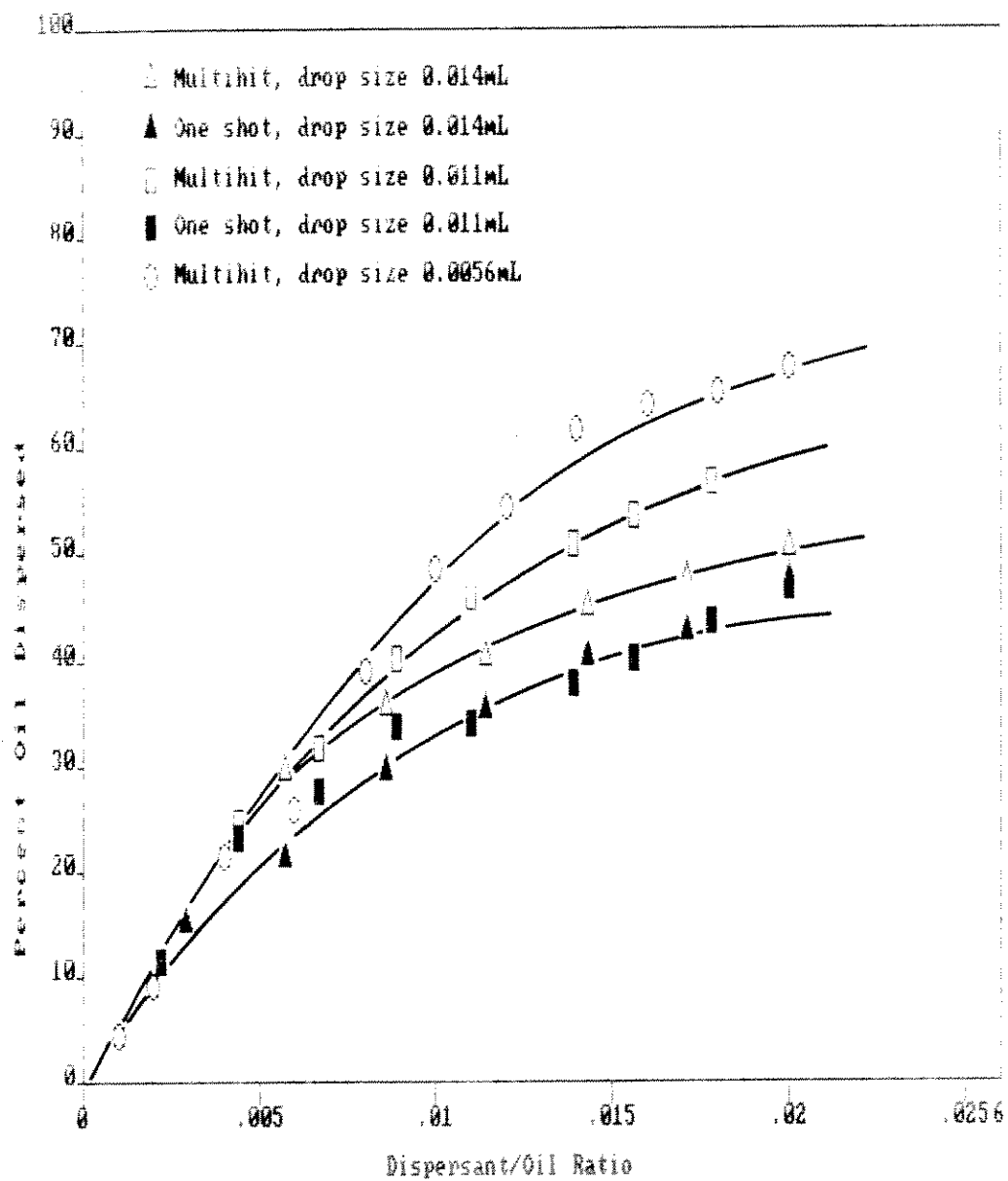
These results support the hypothesis is that to be effective, dispersants must mix or dissolve into the oil and form a solution of

Figure 3.11: Dispersion test - drop size diameter 2.8 mm



Initial oil slick thickness = 0.75 mm, 0.30 mm  
 Dispersant = Corexit 9527  
 Oil = EPS Crude

Figure 3.12: Dispersion test - drop size diameter 0.75 mm



Initial oil slick thickness = 0.75 mm  
 Dispersant = Corexit 9527  
 Oil = EPS Crude

surfactant. This solution must be sufficiently concentrated that there is appreciable partitioning to the interface to reduce its interfacial tension. It must be of sufficient concentration that when an oil drop is sheared off, new dispersant can migrate to the interface and repeat the dispersion process. Presumably this dissolution process is facilitated by the solvents present in the formulation. Small drops with high area to volume ratios are likely to mix more rapidly into the oil. The dispersants are almost invariably denser than the oil thus the drops tend to sink into the oil phase. The rate at which they do this is controlled primarily by the oil viscosity. Observations by Martinelli and Lynch (1980) and others that there is an optimum viscosity for dispersion may be a result of (i) the tendency for dispersant to fall too rapidly through low viscosity oils and thus experience little mixing and (ii) the tendency for dispersant not to penetrate into the oil if the oil is too viscous. In the latter case, it may be washed off or roll off.

One approach towards quantifying effectiveness may be to estimate the extent of dissolution of dispersant drops of various sizes when contracted with oils of various properties and slick thicknesses.

A dissolution rate could be postulated as being the product of some penetration or dissolution velocity  $K$  and drop area  $A$ . A drop of diameter  $D$  will thus dissolve at a rate  $KA \text{ m}^3/\text{s}$  and will shrink in volume by this rate. It follows that since volume is  $\pi D^3/6$  and area is  $\pi D^2$  the differential equation is

$$dV/dt = d(\pi D^3/6) = -KA = -K\pi D^2$$

$$\text{or } 3D^2 dD/dt = -KD^2$$

$$\text{or } dD/dt = -2K$$

$$\text{or } D = D_0 - 2 Kt$$

where  $D_0$  is the initial drop diameter. This model predicts that diameter will shrink linearly with time. The drop volume will thus fall according to

$$V = \pi D^3/6 = \pi (D_0 - 2 Kt)^3/6 = V_0 (1 - 2 Kt/D_0)^3$$

where  $V_0$  is the initial dispersant drop volume ( $\pi D_0^3/6$ ).

If exposure to dissolution is for a time  $T$  then the volume of dispersant dissolved will be  $(V_0 - V)$  or  $V_0 (1 - (1 - 2 KT/D_0)^3)$

The fraction of dispersant dissolved will be this quantity divided by  $V_0$  or,

$$1 - (1 - 2 KT/D_0)^3$$

The maximum value of unity will be reached when  $2 KT$  equals  $D_0$ .

This equation suggests that the critical variable is the dimensionless group  $2 KT/D_0$  consisting of the dissolution "velocity"  $K$ , the drop diameter  $D_0$  and the available dissolution time  $T$ , provided that the time is less than  $D_0/2 K$ . If the drop dissolves completely i.e.  $2 KT/D_0$  exceeds 1 the dissolution time becomes unimportant. If it is completely dissolved i.e.  $2 KT/D$  is less than 1.0 the time is unimportant and effective dispersion is expected.

The obvious approach for estimating the dissolution time is to invoke Stokes' Law that

$$U = gD^2\Delta\rho/18\mu$$

where U is velocity g is the gravitational constant, D is diameter,  $\Delta\rho$  is density difference and  $\mu$  is oil viscosity. But D changes with time as described above thus the drop falling velocity is reduced and may eventually become zero when it vanishes.

The analysis becomes complicated because D falls with time and it is also likely that K is dependent on velocity. It should be possible to set up the differential equation in diameter, velocity, penetration depth and time and solve it numerically. Inspection of the nature of this equation indicates that dispersant drop diameter, slick thickness and oil viscosity will be the critical variables. The aim of dispersant application is to maximize the group  $2KT/D_0$ , i.e. force it as close to 1.0 as possible since this ensures a high proportion of dissolution.

These model-derived deductions are entirely consistent with observations of dispersant effectiveness. This consisting suggests that the modeling approach has validity and the promise of elucidating the nature of the phenomena which control dispersant effectiveness.

It is recommended that experiments be designed to test this mixing dissolution hypothesis. It is possible that positive results could yield a significant improvement in understanding of the nature of the factors influencing dispersant effectiveness.

#### 4. CONCLUSIONS

This study has shown that the double-tube system is convenient for both viewing the dispersion process and for determining the effectiveness of dispersants. A novel method of generating small dispersed drops has been derived.

The results show that small drops of dispersant are more effective tend to confirm the existence of two dispersing regimes with a transition occurring at a particular oil slick thickness.

Some preliminary assessment has been made of the role of dispersant-oil miscing phenomena from which it is included that fundamental study of this phenomena is desirable.

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